

Pyrolysis of energy crops including alfalfa stems, reed canarygrass, and eastern gamagrass [☆]

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Abstract

Production of energy from renewable biomass resources would reduce atmospheric CO₂ increase associated with fossil fuel use. The objective of this study was to evaluate the energy potential of a thermochemical conversion platform of three herbaceous biomass crops. The biomass crops tested were stems of alfalfa, a legume, and whole herbage of reed canarygrass and eastern gamagrass, cool- and warm-season grasses, respectively. Two stages of physiological development were included for the alfalfa and reed canarygrass; bud and full flower stages for the alfalfa, and vegetative and ripe seed stages for the reed canarygrass. The eastern gamagrass was fully mature, senescent material. Pyrolysis products at 600–1050 °C were characterized for gas and char yields, and non-condensable gas product composition. Gas yields ranged between 15 and 36 Nm³ kg^{−1} while char yield ranged between 5.4 and 26.7 wt% of dry initial biomass. Gas yields for alfalfa were greater than from the grasses at all temperatures ranging from 25 to 36 Nm³ kg^{−1} compared to the grasses in the combined range of 15–27 Nm³ kg^{−1} biomass. For the alfalfa stems, the more mature sample yielded more gas. For reed canarygrass, higher gas yield was obtained for the sample harvested at the vegetative stage than the more mature flowering stage. Char was greater for mature reed canarygrass than eastern gamagrass at temperatures of 900 °C or less, with the other biomass samples being intermediate. Maturity effect on alfalfa char yield was not significant. However, all samples had similarly low char residues at 1050 °C. With regard to the composition of non-condensable gas produced, the grasses had higher heating values than alfalfa; however, at 900 °C where the gas heat of combustion is maximized the calorific value of the gas was similar for all samples at about 13.6 MJ kg^{−1}. This compares to about 18.4 MJ kg^{−1} of the parent biomass i.e., about 75%. The activation energy for thermal decomposition, estimated from first order reaction kinetic models, did not exhibit a consistent trend with maturity, but mean activation energy was lower for alfalfa (2837 kJ mol^{−1}) than the grasses (3427 and 3419 kJ mol^{−1} for reed canarygrass and eastern gamagrass, respectively). The effect of maturity on the pyrolysis response was more pronounced for alfalfa than for reed canarygrass. This information aids evaluation and comparison of alternative conversion platforms identified under the US National Biomass Initiative.

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1. Introduction

Current conversion technologies under development for the US Biomass Initiative are based on sugar and thermochemical platforms. Although thermochemical conversion appears to show nearer-term promise for biomass conversion to energy, much of the focus has been on developing integrated biorefineries under the sugar platform. The sugar platform requires various enzymatic reactions which

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are different for each biomass substrate. Some biorefinery stakeholders are showing more interest in thermochemical route as a viable alternative or as a major component of the ethanol refinery process [1]. Pyrolysis is the first step that defines thermochemical conversion and characterizes the product yield into condensable tars, non-condensable gas (which will be known in commercial production as synthetic gas, syngas), and char. Pyrolysis and catalytic pyrolysis can result in as much as 45–62% condensable gas, about 12–25% non-condensable gas and 15–26% char [2]. The oil intermediates, with a calorific value of about 55% that of diesel fuel oil on volume basis [3], constitute various fractions from pyrolytic lignin, organic acids, sugars, and other oxygenated organic compounds that can subsequently be refined to form valuable chemicals and energy carriers, including hydrogen. Besides hydrogen production, neat phenol–formaldehyde resins can also be made from the phenol functionalities of the pyrolysis oils [4]. The non-condensable gas can be converted to mixed alcohols (methanol, ethanol, etc.) via processes similar to the Fischer Tropsch process [1,5,6] or can serve as direct combustion fuel, or supplemental fuel in boilers at ethanol plants.

The role of the biomass feedstock in achieving economic competitiveness with fossil fuel has been well researched [1]. At the moment biomass gasification, including steam reform, is considered uneconomical compared to fossil fuel. While some of the reasons may be attributable to the logistics of harvesting, transporting, and preprocessing biomass, feedstock availability plays a major economic role. It has been established [7] that the economics of thermochemical conversion improve with cultivation and use of dedicated energy crops. Potential energy crops include legumes such as alfalfa and various clovers, cool-season grasses such as reed canarygrass and wheatgrass, and warm-season grasses such as switchgrass, eastern gamagrass and bermudagrass. For example, US production of alfalfa averaged 3.8–19.0 Mg ha⁻¹ on 9.5 million ha during 2000–2003, contributing over \$7 billion to the US economy [8]. Alfalfa stem, the least digestible component of the plant for livestock, constitutes about 50% of the crop biomass and has a large potential as a source of bioenergy. It has been estimated that the potential for ethanol production from switchgrass in the Midwestern United States could yield over 4500 L ha⁻¹ compared with about 3300 L ha⁻¹ for corn grain [8,9]. However, the problem with ethanol production from lignocellulosic saccharification and fermentation is that the residues, unlike distillers dry grains with solubles (DDGS) remaining after corn processing, are not suitable for animal or human consumption. Pyrolysis is a potential solution for utilizing lignocellulosic feedstocks more completely.

In the study reported here, we evaluated the thermochemical energy potential of three potential herbaceous biomass crops; alfalfa, reed canarygrass, and eastern gamagrass. The impact of physiological stage of development on response to pyrolysis yield was also examined in two

of the candidate biomass species, alfalfa and reed canarygrass.

2. Experimental

The alfalfa and reed canarygrass biomass samples utilized in the current study were both collected at two stages of maturity. A more complete description of the alfalfa and the reed canarygrass samples was provided by Dien et al. [10]. Briefly, alfalfa was harvested from 2 yr old stands at Becker and Rosemount, MN when the alfalfa had reached the bud (unopened flower buds present) and full flower (open flowers on all stems) stages of development. The reed canarygrass was harvested from established stands at Arlington, WI at the vegetative stage of development, before elongation of the reproductive stem, and when ripe seed was present. Both of these species were sampled in 2003. The eastern gamagrass sample was dead, fully mature standing herbage collected in the spring of 2003 at State College, PA after snow melt. The biomass samples were air dried and the alfalfa samples were hand separated into leaf and stem fractions, with only the stem fraction being retained for subsequent analysis. Whole herbage from the two grass species was retained for the study. The dried materials were ground with a Wiley mill through a 1- or 2-mm screen prior to analysis. The biomass samples were analyzed for cell wall concentration and composition [10].

A CDS Analytical (Oxford, PA) Pyroprobe was used for the pyrolysis. It consisted of a 1-cm quartz tube heated by a platinum filament of 2–3 mm diameter, and which is capable of maintaining up to 1200 °C temperature at a heating rate of 20 °C/ms. Pulverized samples were sifted and particle sizes with 90% passing a 500 µm screen were used for the pyrolysis experiments. The average weight charged into the pyrolyzer (PY) was about 1 mg and occupied about 1–1.5 mm in height in the quartz tube holder over packed quartz wool. Helium, the carrier gas for the GC/MS, was also used to purge off air in the sample prior to pyrolysis and to purge the pyrolysis gas yield to vent and to the GC. Although the nominal heating rate for the pyroprobe is about 20 °C/ms the sample heating rate can be much lower and is typically estimated at 300 °C s⁻¹ [11]. The experimental sample preparation procedure is reported in [2] and consistent with others reported in the literature [11] which suggest that using samples weighing less than 2 mg does not significantly change gas yield [11]. The pyrolyzer was interfaced to a HP 6890 N gas chromatograph and HP 5973 mass spectrometer (Agilent Technologies). With the pyroprobe/gas chromatograph/mass-spectrometer (PY-GC/MS) system a variety of compounds formed during flash pyrolysis could be characterized. Pyrolyzed non-condensable gas products were separated using a fused silica CP-PoraBOND Q, 25 m × 0.25 mm capillary column (Varian, Palo Alto, CA). The GC was programmed to maintain 35 °C for 3 min after injection, followed by a 5 °C/min ramp to 150 °C, then by a 10 °C/min ramp to 250 °C, for a total time of 36 min. The MS detection was

by electron impact ionization in a full scan mode from $m/z = 2$ to 80 with a threshold at 300. Further description of the equipment, instrumentation, and experimental protocol is given elsewhere [2]. The yields of the major non-condensable gas products from primary and secondary pyrolysis reactions were quantified by calibration with a standard gas mixture consisting of CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₈, and C₄H₁₀ in helium (custom-mixed by Scott Specialty Gases, Plumsteadville, PA). Gas yields were quantified based on a linear relationship between the mass and area counts of the programs (Fig. 1). The R^2 for the linear fits were greater than 0.99 for all gases quantified. Char yield was determined gravimetrically. All other gases, including the condensable gases such as reaction water and pyrolytic oil vapors, plus the non-condensable gases that were not calibrated, were considered as “tar”. These could include hydrocarbon gases greater than C₄ and hydrogen, which was not detected due to equipment limitations. The condensable gas yield was calculated as the difference between the biomass pyrolyzed and the sum of the measured gases and the residual char on mass basis.

Each of the five biomass samples was subjected to a set of pyrolysis temperature and time conditions arranged in a factorial design. Four temperatures (600, 750, 900, and 1050 °C) were evaluated with five lengths of heating (1, 2, 3, 5, 10, and 20 s). For each biomass sample, pyrolysis

experiments were carried out in duplicate at each time and temperature combination.

3. Results and discussion

3.1. Compositional analysis

In herbaceous biomass crops the cellulose, hemicellulose, and lignin polymers in the plant cell wall are the most abundant organic constituents. Table 1 presents the concentrations of cellulose, hemicellulose, and lignin of the five biomass samples used in this study. Also presented are the gross calorific values (GCV) of the biomass samples. The GCVs were similar to other lignocellulosic biomass [12] and the differences amongst samples harvested at different maturity stages appeared small. A more complete compositional analyses, including soluble sugars, carbohydrates, protein, lipids, organic acids, and ash, for the alfalfa and reed canarygrass samples is published previously [10]. For both alfalfa and reed canarygrass, concentrations of cellulose, hemicellulose, and lignin increased with maturity. The increases in cellulose, hemicellulose, and lignin from the immature stage to a more mature stage of development for the reed canarygrass were more than double that for the alfalfa stems. In Dien et al.'s study [10], the alfalfa stems and the reed canarygrass samples were subjected to

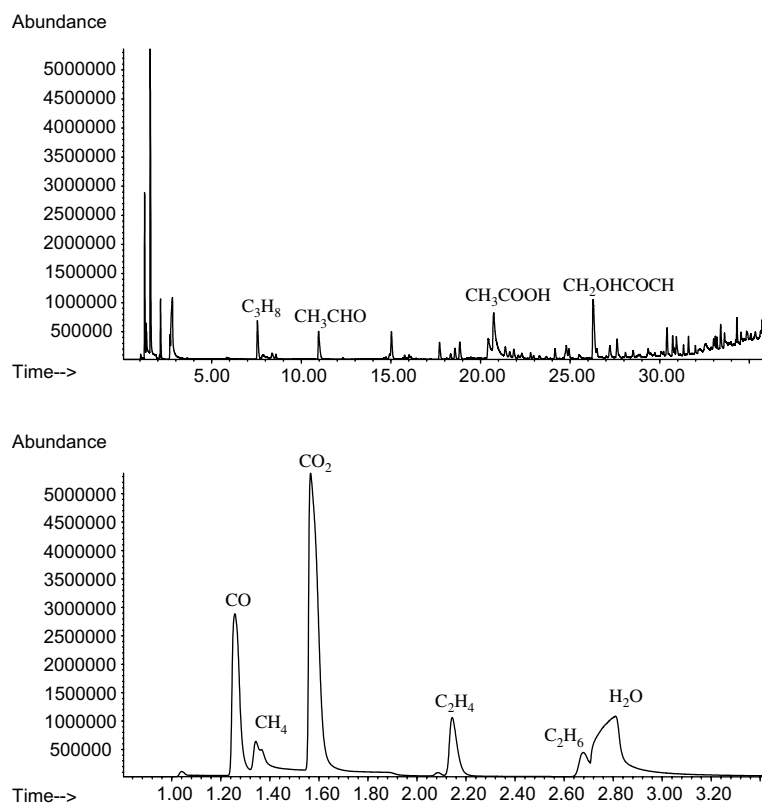


Fig. 1. Typical pyrograms of the chromatography for reed canarygrass at 900 °C. The bottom figure is expanded to show details of the non-condensable gas that was quantified and reaction water that becomes part of condensable gas not quantified.

Table 1

Chemical composition of alfalfa stem and whole herbage reed canarygrass and eastern gamagrass biomass samples used in the pyrolysis experiment

Species	Maturity	Cellulose (g kg ⁻¹ DM)	Hemicellulose (g kg ⁻¹ DM)	Lignin (g kg ⁻¹ DM)	Crude protein ^a	Gross energy (MJ kg ⁻¹)
<i>Alfalfa</i>						
ALF1	Bud	275	205	158	127	18.46
ALF2	Full flower	306	217	175	88	18.74
<i>Reed canarygrass</i>						
RCG1	Vegetative	209	175	109	88	17.70
RCG2	Ripe seed	265	218	148	45	17.64
<i>Eastern gamagrass</i>						
	Ripe seed, over-wintered	335	284	164	NA ^b	18.68

^a From Dien et al. [10].^b Not available.

dilute acid pretreatment and enzymatic saccharification. It was shown that glucose release was substantially greater for the immature reed canarygrass sample than for the mature grass and both alfalfa samples. It was also shown that protein was higher at the immature stages of the biomass than for the matured stages, and within stages, it was higher for alfalfa than the reed canarygrass. Fractional protein composition for gamagrass was not measured. For biomass conversion via the sugar platform, it is well known that cellulose conversion can be negatively impacted by hemicellulose and lignin [13]. On the other hand, lignin is known to improve thermochemical energy conversion efficiency [2]. It might be suggested, therefore, that the increased lignin concentration associated with plant maturity will positively impact pyrolysis product yield.

While the biomass samples used in this study are broadly representative of alfalfa, reed canarygrass, and eastern gamagrass, care must be exercised to not over-interpret the compositional data or the pyrolysis results. It is well established that genetic background of individual biomass species, stage of physiological development when harvested, and the environment in which the species grew will all significantly impact chemical composition of the harvested material [14]. Because only single samples of each biomass species, at any stage of maturity, were included in this study, the observed differences among samples must be considered as being preliminary estimates that must be verified with larger sets of biomass samples that incorporate these known sources of possible variation.

3.2. Non-condensable gas yield

Fig. 1 presents typical pyrograms of the chromatography from which the non-condensable gases were quantified. A typical time-dependent yield of the non-condensable gas is shown in Fig. 2 indicating that the kinetics is fast and that by about 5 s the reaction is complete. Except for the kinetics of the conversion which is discussed later, discussion on total gas and char yields as functions of temperature is based on the pyrolysis times when conversion has completed. Fig. 3 presents the non-condensable gas yields for the biomass samples as a func-

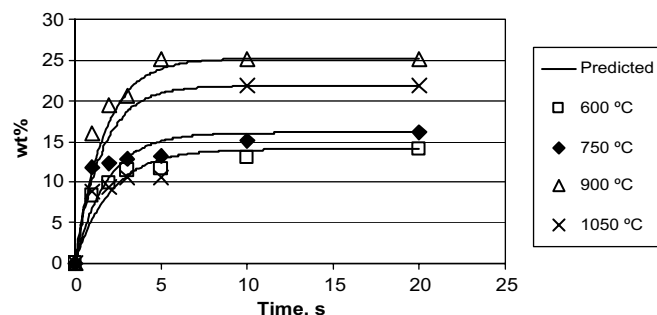


Fig. 2. Typical conversion vs. time curves shown for RCG1. Fitted curves are based on activation energy and frequency factors estimated from first order kinetics models of syngas production.

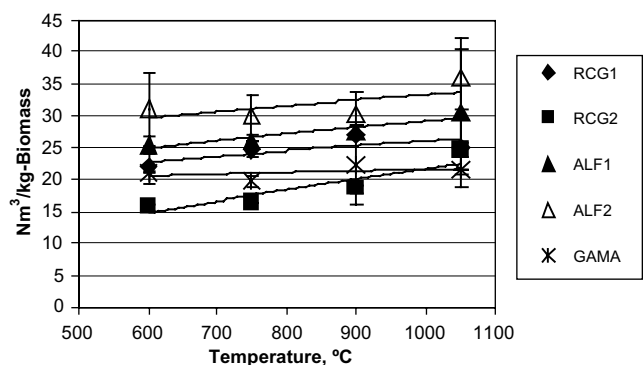


Fig. 3. Non-condensable gas yields (wt% of biomass dry mass) at final pyrolysis time for bud and full flower stage alfalfa samples (ALF1 and ALF2, respectively), vegetative and ripe seed stage reed canarygrass (RCG1 and RCG2, respectively), and eastern gamagrass (GAMA). Error bars are standard deviation from the mean values of final pyrolysis yields at 10 and 20 s. These are fitted to power curves with R^2 of 0.67 for RCG1, 0.91 for RCG2, 0.99 for ALF1, 0.83 for ALF2 and 0.81 for GAMA.

tion of pyrolysis temperature at the heating time where maximal yields were achieved i.e., 10 and 20 s. All five biomass samples exhibited similar responses of increasing non-condensable gas yield with increasing temperature with similar slopes. The more mature alfalfa stems appeared to give the highest yields while the mature reed canarygrass had the lowest yields at most temperatures except at 1050 °C where mature reed canarygrass overlapped the

eastern gamagrass. The non-condensable gas yields for the immature alfalfa stem, the mature reed canarygrass, and eastern gamagrass samples were broadly similar. The effect of maturity on non-condensable gas yield was inconsistent. For the alfalfa stems, the more mature sample yielded more gas than the immature sample whereas the opposite effect was observed for reed canarygrass.

It has been observed that during the pyrolysis of biomass hemicellulose decomposes before cellulose while lignin decomposition occurs throughout the process [15]. However the amount of gas evolved does not necessarily contribute to non-condensable gas yield as some may be released as condensable gases (bio-oils). While bio-oil is typically a mixture of many organic compounds it is mostly classified as acids, alcohols, aldehydes, anhydrosugars, furans, ketones, etc. derived from the carbohydrate fraction and aldehydes, aromatic acids, and phenolic compounds derived from the lignin fraction [16]. Devolatilization of biomass begins around 250 °C for hemicellulose and by 400 °C the primary decomposition reactions are complete [17]. It has been reported that the condensable gases that make up bio-oils are maximized at 500 °C [5], but beyond that e.g., the temperatures we studied the rate of evolution and breakdown of the stronger C=C bonds and the cracking of the higher molecular weight tars and char occur thereby resulting in higher yields of non-condensable gas we observed.

3.3. Char yield

Char yield was a function of pyrolysis temperature. All biomass samples showed a decline with increasing temperature in residual char after pyrolysis; however, the patterns deviated among samples (Fig. 4). Mature reed canarygrass had the greatest reduction in char associated with increasing pyrolysis temperature while eastern gamagrass had the least response to temperature for char yield. The other three biomass samples were intermediate in response. At 1050 °C, pyrolysis appeared to be complete for all the bio-

mass samples as the char remaining was approximately the same for all samples, regardless of species or maturity. After primary decomposition which takes place at relatively lower temperatures, secondary reactions involving char pyrolysis takes place at elevated temperatures. The char remaining after complete devolatilization is a reflection of total gas yield, condensable and non-condensable.

As Fig. 1 indicates, the condensable gases can comprise all the gases that were not quantified including H₂ and include the reaction water, organic acids, aldehydes, alcohols, sugars, etc. This can be estimated by the difference between the sample weight and sum of the char and quantified non-condensable gas. The condensable gases by this definition generally increased with increased temperature (Fig. 5).

3.4. Gas composition

In gasification the primary combustibles in the non-condensable gas (syngas) comprises CO, H₂, and low molecular weight hydrocarbons (HC). Syngas can be used as primary fuel for direct combustion or can be further processed to Fischer Tropsch liquids [6]. Further analysis of the non-condensable gas was needed to evaluate the gas quality. In Fig. 6 we present the major components of the non-condensable gas produced by pyrolysis at various temperatures for times between 10 and 20 s when pyrolysis is complete. These included CO, CO₂ and the low molecular weights hydrocarbon gases CH₄, C₂H₄, C₂H₆, C₃H₈, and C₄H₁₀. As mentioned earlier, H₂ was not quantified due to lack of an appropriate detector in the current PY-GC/MS system, however, its yield and evolution trends are known to be consistent with CO on a molar basis [18]. It is important to quantify CO₂ because its presence will decrease syngas quality unless it can be converted to combustible gas products. As Fig. 6 shows, the CO₂ component of the produced gas was highest at lowest temperature (600 °C) for all biomass samples regardless of species or maturity, and decreased with increasing pyrolysis temperature. Because both CO and the hydrocarbons (HC)

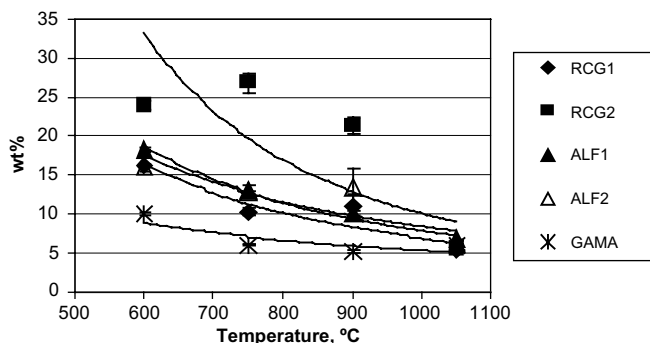


Fig. 4. Char remaining after final pyrolysis time of 20 s for bud and full flower stage alfalfa samples (ALF1 and ALF2, respectively), vegetative and ripe seed stage reed canarygrass (RCG1 and RCG2, respectively), and eastern gamagrass (GAMA). Error bars are standard deviation from the mean values. The data are fitted to power curves with R^2 of 0.82 for RCG1, 0.58 for RCG2, 0.98 for ALF1, 0.69 for ALF2 and 0.68 for GAMA.

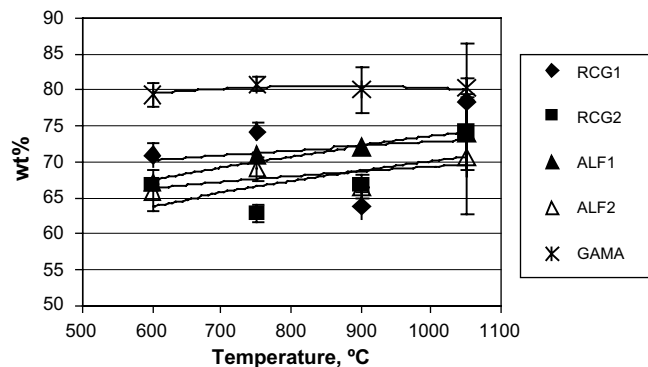


Fig. 5. Condensable gas determined by difference between biomass sample weight and the sum of non-condensable gas and char remaining after pyrolysis.

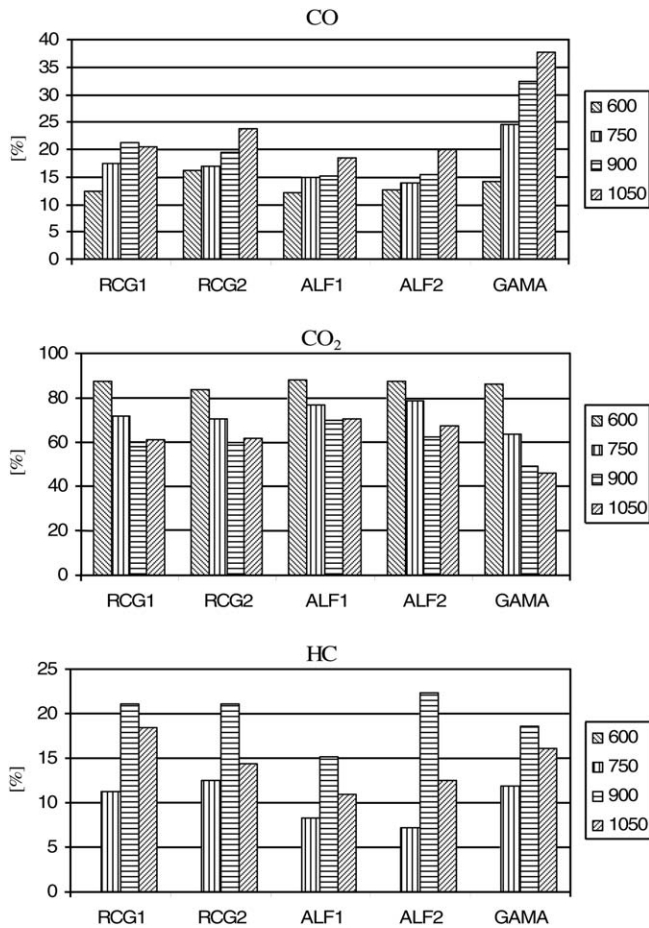


Fig. 6. Percent composition of quantified non-condensable gas yielded.

trended upward with temperature, syngas quality should improve with pyrolysis temperature for all samples. The rate of CO increase with pyrolysis temperature was gradual and limited for alfalfa and reed canarygrass (from approximately 12% at 600 °C to 24% at 1050 °C), whereas eastern gamagrass had substantially greater increases in CO percentage with pyrolysis temperature (from 14% at 600 °C to 38% at 1050 °C). The impact of maturity was not large for CO for either alfalfa or reed canarygrass. Fushimi et al. [19] suggested that about 80% of cellulose would have been depolymerized at 500 °C, just below the minimum temperature of 600 °C that we studied. Unlike cellulose, CO evolution from lignin begins at a low pyrolysis temperature but increases rapidly thereafter.

The composition of the hydrocarbon fraction consisted mainly of CH₄ with small amounts of C₂₋₄H_x. The hydrocarbon fraction increased with temperature, consistent with the depolymerization of larger molecular weight hydrocarbons (i.e., tars, greater than C₄) which would otherwise condense to form part of the bio-oil constituent. Unlike cellulose, where CO evolution is followed by the onset of H₂ formation, the evolution of CO from lignin is followed by CH₄ formation [11]. Given the increases in lignin with plant maturity, one would expect the gas combustibility to improve with pyrolysis temperature. The percentage of

the primary combustible components of the syngas (CO and low molecular weight hydrocarbons) peaked at 900 °C for all biomass samples.

3.5. Cold gas efficiency

One of the potential benefits of gasification in the bio-refinery process stream is when it can be co-located with ethanol plants to provide alternative energy to fossil fuels. Currently the only thermochemical conversion technologies in ethanol plants are direct-fired combustion systems. However, combustion of the syngas derived from a gasifier may offer a cleaner and more efficient thermal conversion than directly burning the biomass. Additionally, in installations where the objective of the pyrolysis is to produce bio-oils from the condensable gas the associated non-condensable gas becomes a potential source of energy for the reactor. It was deemed important in this study to evaluate the heat of combustion of the non-condensable gas and compare it with the GCV of the parent biomass. The gross energy of the syngas was calculated based on the heat of combustion of the gas components shown in Fig. 6 and the results are presented in Fig. 7. As the figure shows, the syngas gross energy peaks around 900 °C for all but immature alfalfa stems, reaching almost the same at about 13.6 MJ kg⁻¹. The relationship between pyrolysis temperature and the heating values were fitted to a second degree polynomial as follows:

$$\text{GAMA}_{\text{HHV}} = -0.0222T^2 + 42.716T - 17316 \quad R^2 = 0.99 \quad (1)$$

$$\text{RCG1}_{\text{HHV}} = -0.02227T^2 + 42.644T - 17387 \quad R^2 = 0.98 \quad (2)$$

$$\text{RCG2}_{\text{HHV}} = -0.0265T^2 + 48.709T - 19355 \quad R^2 = 0.98 \quad (3)$$

$$\text{ALF1}_{\text{HHV}} = -0.0182T^2 + 33.75T - 13474 \quad R^2 = 0.97 \quad (4)$$

$$\text{ALF2}_{\text{HHV}} = -0.0237T^2 + 44.081T - 17827 \quad R^2 = 0.81 \quad (5)$$

To compare the heating value of the gas with the parent biomass we define cold gas efficiency as the ratio of the gas heating value to that of the parent biomass and is stated as [20],

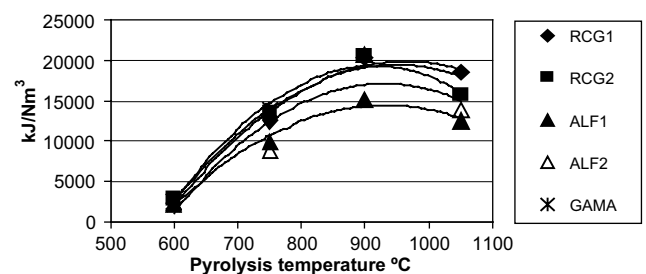


Fig. 7. Heating value of non-condensable produced gas quantified. Value does not include excluding H₂.

Table 2

First order reaction rate kinetic constants established using parameter estimation model for the total non-condensable gas

	A (s^{-1})	E ($kJ\ mol^{-1}$)
<i>Alfalfa</i>		
Bud (ALF1)	1.2672	3957.63
Full flower (ALF2)	1.3150	1718.00
Average	1.2911	2837.82
<i>Reed canarygrass</i>		
Vegetative (RCG1)	1.080	5837.76
Ripe seed (RCG2)	0.7486	1017.83
Average	0.9143	3427.80
Eastern gamagrass (GAMA)	1.0644	3418.82

$$\eta_g = \frac{\sum([HHV]_{gi} \times wt\%_{gi})}{[GCV]_b} \times 100\% \quad (6)$$

where $[HHV]_g$ ($MJ\ kg^{-1}$) is the heat of combustion of the product gas component, $wt\%$ is the weight percent of the component gas in the produced gas, while $[GCV]_b$ is the biomass gross calorific value determined experimentally. The most efficient non-condensable gas production was at $900\ ^\circ C$. At this peak temperature the HHV was about the same for all biomass samples and cold gas efficiency was about 75%.

3.6. Kinetics of gas evolution

The kinetics of gas evolution was evaluated using first order reaction kinetics. The generalized model may be represented by

$$\frac{dm}{dt} = A_0 \exp(-E_m/RT)(m_f - m) \quad (7)$$

where m was the yield of any product of the gases quantified (i.e., CO_2 , CO , CH_4 , C_2H_6 , C_2H_4 , C_3H_8 , or their sum); A_0 was the frequency factor corresponding to product m , $[1/s]$; E_m was the activation energy corresponding to product m [$MJ\ mol^{-1}$]; R was the universal gas constant [$8.314\ kJ\ mol^{-1}\ K^{-1}$]; m_f was the final yield of product “ m ” (in this case after 20 s) and T was the temperature in kelvin (i.e., 873, 1023, 1173, 1323 K). Typical result of the parameter estimation with the first order kinetic model for the pyrolysis reaction and the experimental data was shown in Fig. 2. Agreement appears reasonable given the heterogeneous nature of the reaction, especially at short pyrolysis times. The estimated parameter values are given in Table 2. The activation energies for the immature alfalfa and reed canarygrass samples were substantially higher than the corresponding more mature samples; however, the opposite pattern was found with switchgrass in a previous study [2]. When data were averaged across maturity stages for alfalfa and reed canarygrass, activation energy was lowest for alfalfa stems than the grasses. However, both grasses were similar.

4. Conclusions

The biomass-to-syngas energy conversion for the alfalfa stems and whole herbage of reed canarygrass was greater than observed for an eastern gamagrass whole herbage sample. For alfalfa, the more mature sample yielded more non-condensable gas, but for reed canarygrass no obvious stage of maturity differences were encountered. Gas quality was best for more mature biomass samples at all temperatures studied, but the temperature at which peak yields were obtained occurred at $900\ ^\circ C$ for all samples. The non-condensable syngas components CO and CO_2 products were greatest from the eastern gamagrass. It appears that eastern gamagrass can be a competitive energy crop for thermochemical conversion and deserves more of a look as a bioenergy crop than it has previously received. More research is underway to characterize the maturity effect.

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